Abstract No. mars52

Near-Edge X-ray Absorption Fine Structure Characterization of Polymers Based on 2-Vinyl-4,5-dicyanoimidazole

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Beamline(s): U7A

Introduction: Polymer thin films find use in a variety of interfacial applications. Poly(2-vinyl-4,5-dicyanoimidazole), or polyvinazene, has recently been developed and shows promise for use as a catalytic support or in ion-exchange applications.[1-2] For these applications, it is critical that surface properties be well-understood. In the present work, the surface structure and chemical bonding in thin films of polyvinazene and poly(vinazene-co-styrene) have been characterized using Near Edge X-ray Absorption Fine Structure, or NEXAFS, at the C-K-edge. The results clearly indicate the sensitivity of NEXAFS to chemical structure.

Methods and Materials: Polyvinazene and poly(vinazene-co-styrene) were synthesized by methods previously published.[1] Thin films were prepared by spin coating from 0.5% (w/v) solutions of polyvinazene in acetonitrile and poly(vinazene-co-styrene) in tetrahydrofuran onto 1cm^2 Si substrates. Spectra were collected using partial electron yield (PEY) detection. Resonance assignments were made based on previous work with polystyrene[3] and dicyanoimidazole compounds.[4] No visible damage from exposure to the soft x-ray beam was observed.

Results: The C-K-edge NEXAFS spectrum for polyvinazene is shown in Figure 1. The results show that the surface is composed primarily of the pendant dicyanoimidazole ring. Comparison of spectra taken at two different angles of incidence clearly indicates that the dicyanoimidazole ring is oriented away from the surface normal. This preferential orientation close to the surface plane results from hydrogen-bonding between pendant dicyanoimidazole groups. The C-K-edge NEXAFS spectrum for poly(vinazene-co-styrene) is shown in Figure 2. The results for the copolymer clearly show that the surface is composed primarily of phenyl groups. However, for the copolymer, two distinct pi* resonances are present in the C-K-edge spectrum: one for the phenyl ring and one for the dicyanoimidazole ring. No orientation dependence was observed for spectra taken for the copolymer.

Conclusions: The structure and bonding of functional groups present at the surface of these thin polymer films were successfully probed using NEXAFS. The sensitivity of NEXAFS to chemical structure is illustrated by the ability to spectroscopically distinguish the pendant rings present in the copolymer.

Acknowledgments: A. Marsh would like to thank the National Science Foundation for an IGERT fellowship (grant number DGE-9972776).

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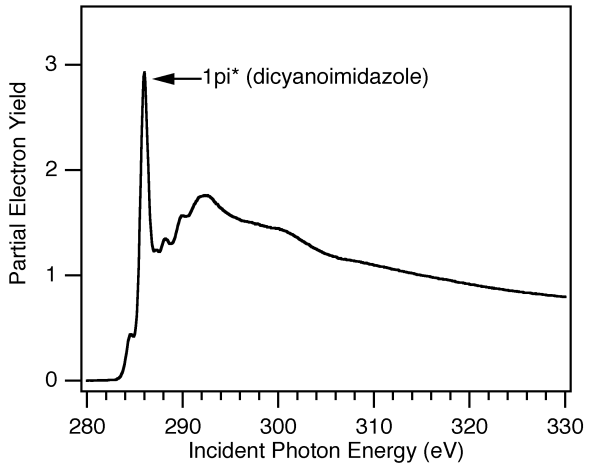

Figure 1. C-K-edge NEXAFS spectrum, taken at normal incidence, of a spin-coated polyvinazene thin film.

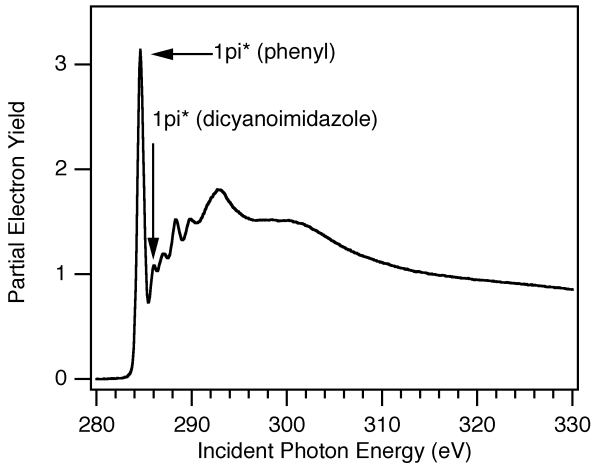

Figure 2. C-K-edge NEXAFS spectrum, taken at normal incidence, of a spin-coated poly(vinazene-co-styrene) thin film.